3154 *Inorg. Chem.* **1986**, *25*, 3154–3157

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Acyclic Polythioether Complexes: Preparation and Crystal Structure of Tricarbonyl(2,5,8-trithianonane)molybdenum(0)

Michael T. Ashby, John H. Enemark,* Dennis L. Lichtenberger,* and Richard B. Ortega

Received September 17, 1985

Tricarbonyl(2,5,8-trithianonane)molybdenum(0) has been prepared and characterized by single-crystal X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 7.255 (3) Å, b = 12.270 (3) Å, c = 15.229 (3) Å, β = 96.51 (2)°, V = 1346.9 (6) Å^3, and Z = 4. The structure was solved by using the heavy-atom Patterson method followed by least-squares refinement using 3039 independent reflections to a final R_1 value of 0.026 (R_2 = 0.031). A detailed comparison is made between the structural and spectroscopic data obtained for tricarbonyl(2,5,8-trithianonane)molybdenum(0) and those previously reported for tricarbonyl(1,4,7-trithiacyclononane)molybdenum(0). This comparison suggests that the sulfur donor orbitals for tricarbonyl(2,5,8-trithianonane)molybdenum(0) are more favorably directed toward the empty metal orbitals than those for tricarbonyl(1,4,7-trithiacyclononane)molybdenum(0).

In recent years there has been considerable interest in the coordination chemistry of mesocyclic[1] polythioethers[2] such as 1,4,7-trithiacyclononane (TTCN).[3-5] Reports of M(TTCN)$_2$ (M = Co(II), Ni(II), Cu(II)) have appeared;[3] however, these compounds do not allow one to completely investigate the distortion of the TTCN ring upon complexation. Consequently, (TTCN)Mo(CO)$_3$ was prepared and structurally characterized by single-crystal X-ray diffraction.[4] The facial configuration of the carbonyl ligands in (TTCN)Mo(CO)$_3$ provides a unique point of reference for describing the trigonal distortion observed in the pseudooctahedral complex. This trigonal distortion is ascribed to mechanical constraints within the mesocyclic TTCN ring that serve to rotate the sulfur donor orbitals away from the molecular 3-fold axis. However, what effect do such constraints have on the electron-donating ability of the polythioether? To address this question, the title compound (TTN)Mo(CO)$_3$, which contains the analogous open-chain trithioether, 2,5,8-trithianonane (TTN), has been prepared and structurally characterized. To our knowledge, this is the first acyclic polythioether–metal complex (more than two sulfur atom donors) to be characterized by X-ray crystallography.[2] Additional impetus for investigating (TTN)Mo(CO)$_3$ comes from a recent report on the use of the molybdenum tricarbonyl fragment as a template for the high-yield synthesis of TTCN.[5]

Experimental Section

Solvents were dried by routine methods.[6] Molybdenum hexacarbonyl (Aldrich) and bis(2-mercaptoethyl) sulfide (Parish) were used as received without further purification.

Preparation of 2,5,8-Trithianonane. To a Schlenk flask was added bis(2-mercaptoethyl) sulfide (1.72 g, 11.2 mmol) and ca. 20 mL of dry THF. After the mixture was degassed with argon, sodium hydride (0.55 g, 22.3 mmol) was added. The resulting slurry was stirred for 30 min, at which time it was cooled to −78 °C and iodomethane (1.40 mL, 3.19 g, 22.5 mmole was added. The mixture was stirred for 15 min and warmed to room temperature, and the reaction was quenched with water. The product was extracted with ether and dried over magnesium sulfate. Vacuum distillation (5 mm, 130–135 °C) gave the product in high yield as a clear colorless liquid: ^{1}H NMR (CD_2Cl_2) 2.73 (m, 8 H, CH_2CH_2), 2.12 ppm (s, 6 H, CH_3).

Table I. Crystallographic Data for (TTN)Mo(CO)$_3$ at 25 °C[a]

(A) Cell Parameters

formula	$C_9H_{14}O_3S_3Mo$	a,[b] Å	7.255 (3)
fw	362.34	b, Å	12.270 (3)
cryst color	pale yellow	c, Å	15.229 (3)
cryst shape	triangular prism	V, Å^3	1346.9 (6)
cryst size, mm	0.5 × 0.4 × 0.3	β, deg	96.51 (2)
cryst orientation	random	Z	4
cryst syst	monoclinic	d_{calcd}, g cm^{-3}	1.787
space group	$P2_1/n$	d_{obsd},[c] g cm^{-3}	1.75 (1)
		μ, cm^{-1}	13.87

(B) Measurement and Treatment of Intensity Data

radiation	Mo Kα (λ = 0.71073 Å), monochromatized by a graphite cryst
data colln method	$\theta/2\theta$ scan
scan speed, deg min^{-1}	variable (2.5–14.5) as a function of reflcn intens
scan range (2θ), deg	Mo Kα_1 = −1.2 to Mo Kα_2 = +1.6
ratio of total bkgd time to peak scan time	0.5
std reflcns	(101), (135), (328) recollcd every 97 reflcns
max deviation of std, %	<2
max 2θ, deg	60
no. of unique data	3957
no. of data used	3039; $I > 3\sigma(I)$
final residuals	
R_1	0.026
R_2	0.031
final GOF	1.29

[a] The estimated standard deviation of the least significant figure is given in parentheses in this table and in the tables that follow. [b] The cell dimensions were obtained from a least-squares refinement of setting angles of 23 reflections in the 2θ range 20–31°. [c] Density was determined by the flotation method in $CHBr_2CHBr_2/CCl_4$.

Preparation of Tricarbonyl(2,5,8-trithianonane)molybdenum(0). Mo(CO)$_6$ (1.00 g, 3.8 mmole was stirred in dry refluxing acetonitrile (ca. 30 mL) under an argon atmosphere for 4 h to give Mo(CO)$_3$(NCCH$_3$)$_3$.[7] To the resulting pale yellow solution was added 2,5,8-trithianonane (0.55 g, 3.0 mmol). The dark yellow solution was refluxed for 1 h to give a brown solution, which was cooled to room temperature, reduced to ca. 20 mL on a rotary evaporator, and filtered through a column of Celite (1.5 × 3.0 cm). The resulting light brown solution was degassed with argon and stored at −5 °C, whereupon light yellow crystals formed. The product was collected on a glass frit, washed with pentane, and dried to give 0.43 g (40% based on TTN): IR ν_{CO}(CH_2Cl_2) 1931, 1821; IR ν_{CO}(nitromethane) 1927, 1815; ^{1}H NMR (CD_2Cl_2) 2.62–2.79 (m, 8 H, CH_2CH_2), 2.42 ppm (s, 6 H, CH_3); ^{95}Mo NMR (nitromethane) −1213 ppm (relative to external 2 M Na_2MoO_4, pH 11), line width 14 Hz. Recrystallization from hot nitromethane gave a sample suitable for elemental analysis. Anal. Calcd for $C_9H_{14}O_3S_3Mo$: C, 29.83; H, 3.90; S, 26.55. Found: C, 29.89; H, 3.89; S, 26.47.[8]

X-ray Crystallography. The crystallographic data for (TTN)Mo(CO)$_3$ are summarized in Table I. A well-formed crystal was selected from

---

(1) "Mesocycle" has been defined as a medium-size ring: Leonard, N. J.; Milligan, T. W.; Brown, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 4075.

(2) For a timely review of thioether transition-metal complexes see: Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

(3) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(4) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636.

(5) Sellmann, D.; Zapf, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 807.

(6) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

(7) Ross, B. L.; Grasselli, J. L.; Richey, W. M.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 1023.

(8) Chemical analysis performed by Atlantic Microlab, Atlanta, GA 30360.

0020-1669/86/1325-3154$01.50/0

Table II. Atomic Coordinates for the Non-Hydrogen Atoms in $(TTN)Mo(CO)_3$

atom	*x*	*y*	*z*
Mo	0.03774 (3)	0.17863 (2)	0.21352 (1)
S1	−0.04285 (8)	0.00654 (5)	0.11944 (4)
S2	−0.27717 (9)	0.23717 (6)	0.14073 (4)
S3	0.1426 (1)	0.25435 (6)	0.06950 (4)
O1	0.1122 (3)	0.3796 (2)	0.3359 (2)
O2	−0.1079 (4)	0.0857 (2)	0.3821 (1)
O3	0.4309 (3)	0.1046 (2)	0.2941 (1)
C1	0.0847 (4)	0.3077 (2)	0.2866 (2)
C2	−0.0565 (4)	0.1183 (3)	0.3180 (2)
C3	0.2845 (3)	0.1307 (2)	0.2621 (2)
C4	−0.1039 (4)	−0.1013 (3)	0.1905 (2)
C5	−0.2648 (4)	0.0330 (3)	0.0561 (2)
C6	−0.3860 (4)	0.1125 (3)	0.0969 (2)
C7	−0.2318 (5)	0.3136 (3)	0.0433 (2)
C8	−0.0684 (5)	0.2762 (3)	−0.0030 (2)
C9	0.2283 (6)	0.3911 (3)	0.0862 (2)

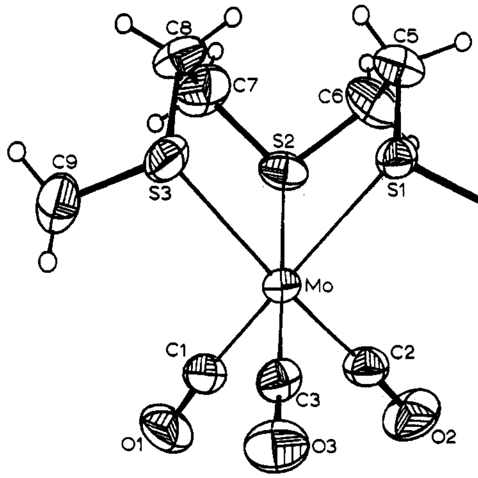


Figure 1. ORTEP side view of the $(TTN)Mo(CO)_3$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the labeling scheme is defined. Hydrogen atoms have been assigned an arbitrary thermal parameter.

those grown from the reaction mixture and mounted on a Syntex $P2_1$ diffractometer. The results from the automatic centering, indexing, and least-squares routines[9] and the axial photographs were consistent with a primitive monoclinic lattice. Data were collected for a unique quadrant to $2\theta = 60°$. Three check reflections monitored every 97 readings showed no significant decay during data collection. The systematic absences were unique to the nonstandard space group $P2_1/n$. The data were corrected for Lorentz and polarization effects assuming that the monochromator crystal was 50% mosaic and 50% perfect. The data were corrected for absorption by the Gaussian integration method.

The structure determination and refinement were carried out with the SDP series of crystallographic programs[10] running interactively on a PDP 11/34a computer. The structure was solved by using the heavy-atom Patterson method. Subsequent difference Fourier techniques were used to locate the remaining non-hydrogen atoms (Table II). After anisotropic refinement, all of the hydrogen atoms, including the methyl hydrogens, were located in a difference electron density map. For the final cycles of refinement, the positional parameters of the hydrogen atoms were varied and their thermal parameters were fixed 1.5 times greater than the value of their bonded carbon. The final cycles converged to give $R_1 = 0.026$, $R_2 = 0.031$, and GOF = 1.287.[11] The largest residual in the final difference electron density map was 0.57 e Å^{-3} and was located near the molybdenum atom.

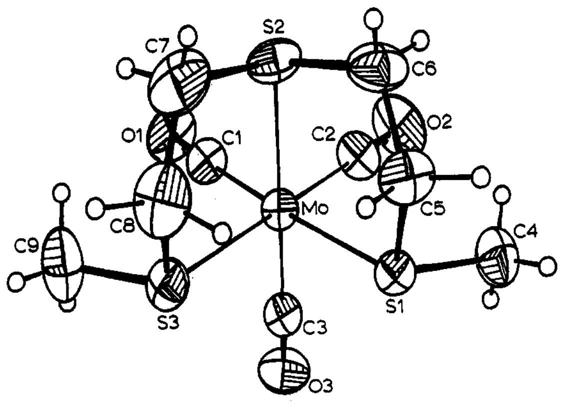


Figure 2. ORTEP top view of the $(TTN)Mo(CO)_3$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the labeling scheme is repeated. Hydrogen atoms have been assigned an arbitrary thermal parameter.

Table III. Selected Bond Distances (Å) in $(TTN)Mo(CO)_3$

Mo–S1	2.581 (1)	S1–C4	1.797 (3)	O1–C1	1.161 (3)
Mo–S2	2.528 (1)	S1–C5	1.810 (3)	O2–C2	1.156 (3)
Mo–S3	2.575 (1)	S2–C6	1.813 (3)	O3–C3	1.162 (3)
Mo–C1	1.943 (2)	S2–C7	1.817 (4)	C5–C6	1.495 (4)
Mo–C2	1.947 (2)	S3–C8	1.802 (3)	C7–C8	1.517 (5)
Mo–C3	1.949 (2)	S3–C9	1.798 (3)		
S1··S2	3.336 (1)	S2··S3	3.353 (1)	S1··S3	3.445 (1)

Table IV. Selected Bond Angles (deg) in $(TTN)Mo(CO)_3$

S1–Mo–S2	81.52 (2)	Mo–S1–C5	106.32 (9)
S1–Mo–S3	83.83 (2)	C4–S1–C5	100.8 (2)
S1–Mo–C1	176.79 (7)	Mo–S2–C6	104.8 (1)
S1–Mo–C2	93.67 (8)	Mo–S2–C7	105.4 (1)
S1–Mo–C3	95.97 (7)	C6–S2–C7	104.3 (2)
S2–Mo–S3	82.15 (2)	Mo–S3–C8	105.2 (1)
S2–Mo–C1	96.34 (7)	Mo–S3–C9	110.3 (1)
S2–Mo–C2	94.73 (7)	C8–S3–C9	101.8 (2)
S2–Mo–C3	176.28 (6)	Mo–C1–O1	174.6 (2)
S3–Mo–C1	98.27 (7)	Mo–C2–O2	177.1 (2)
S3–Mo–C2	176.25 (7)	Mo–C3–O3	177.2 (2)
S3–Mo–C3	94.87 (6)	S1–C5–C6	115.2 (2)
C1–Mo–C2	84.1 (1)	S2–C6–C5	116.9 (2)
C1–Mo–C3	86.3 (1)	S2–C7–C8	116.5 (2)
C2–Mo–C3	88.2 (1)	S3–C8–C7	114.5 (2)
Mo–S1–C4	108.9 (1)		

Table V. Selected Torsion Angles (deg) in $(TTN)Mo(CO)_3$[a]

C4–S1–C5–C6	87.0	C6–S2–C7–C8	−76.3
S1–C5–C6–S2	46.0	S2–C7–C8–S3	−48.3
C5–C6–S2–C7	−70.9	C7–C8–S3–C9	79.9

[a] Torsion angles for A–B–C–D are defined as positive for clockwise rotation of C–D toward A–B, looking down the B–C bond.

Results and Discussion

The method of preparation of $(TTN)Mo(CO)_3$ from $Mo(CO)_3(NCCH_3)_3$ was similar to that used to prepare $(TTCN)Mo(CO)_3$.[4] A related compound, $(TTU)Mo(CO)_3$ (TTU = 3,6,9-trithiaundecane), has been prepared directly from $Mo(CO)_6$ and the corresponding free polythioether under somewhat more vigorous conditions.[12] The carbonyl stretching frequencies for $(TTN)Mo(CO)_3$ are similar to those reported for $(TTCN)Mo(CO)_3$,[4] $(TTU)Mo(CO)_3$,[12] and other $Mo(CO)_3$ complexes with S-donor ligands.[13] The ^{95}Mo chemical shift is comparable to that reported for $(TTCN)Mo(CO)_3$.[4] $(TTN)Mo(CO)_3$, like (TTC-

---

(9) Programs used on the diffractometer were written by Syntex Analytical Instruments (now Nicolet XRD Corp.), Cupertino, CA.

(10) Programs used on the PDP 11/34a computer: The Structure Determination Package (SDP) (B. A. Frenz & Associates Inc., College Station, TX and Enraf-Nonius, Delft, Holland) and ORTEP 2 (Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory, Oak Ridge, TN). ORTEP 2 is included in the SDP software package.

(11) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wf_o^2]^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where *n* is the number of reflections used in the refinement, *m* is the number of variable parameters, and $w = 4F_o^2/[\sigma^2(F_o)^2 - (pF_o^2)^2]$ where *p*, the factor to prevent overweighting of the strong reflections, was set equal to 0.03.

(12) Mannerskantz, H. C. E.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4454.

(13) Cotton, F. A.; Zingales, F. *Inorg. Chem.* **1962**, *1*, 145.

Table VI. Comparison of Selected Structural Features of $(TTCN)Mo(CO)_3$ and $(TTN)Mo(CO)_3$

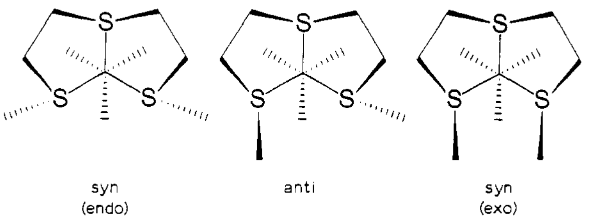
	$(TTCN)Mo(CO)_3$	$(TTN)Mo(CO)_3$[a]	
	Distances (Å)		
S··S′	3.354 (8)	3.35 (1)	3.445 (1)
Mo–S	2.52 (2)	2.578 (4)	2.528 (1)
	Angles (deg)		
C–S–C′	103.0 (9)	101.3 (7)	104.3 (2)
	Torsion Angles (deg)		
S–C–C′–S′	48 (2)	47 (2)[b]	

[a] For $(TTN)Mo(CO)_3$, the first number is an average value of the distances or angles related by the noncrystallographic mirror plane. [b] Average of the absolute value of the mirror-related torsion angles.

N)$Mo(CO)_3$, is unaffected by short-term exposure to air; however, some decomposition occurs upon long-term storage (6 months). The decomposition products smell of free TTN.

A side view of the $(TTN)Mo(CO)_3$ molecule is shown in Figure 1 and a top view is shown in Figure 2. Pertinent interatomic distances, interatomic angles, and torsion angles are summarized in Tables III–V, respectively.

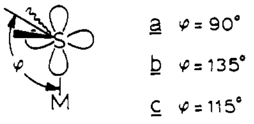
The features of most interest in this structure are those that describe the contrasting differences between TTN and its cyclic analogue TTCN. Table VI compares the crystal structure results for $(TTCN)Mo(CO)_3$ with those obtained for $(TTN)Mo(CO)_3$. The molecular structure of $(TTN)Mo(CO)_3$ is substantially the same as that reported for $(TTCN)Mo(CO)_3$,[4] a pseudooctahedral coordintion complex with three facial carbonyl ligands and three trans thioether donor ligands. A fundamental difference between the molecular structure of $(TTCN)Mo(CO)_3$ and $(TTN)Mo(CO)_3$ is that the former possesses approximate C_3 symmetry and the latter possesses approximate C_s symmetry. Furthermore, only one regioisomer (and two conformers) are possible for $(TTCN)Mo(CO)_3$; however, in principle three regioisomers (and ten conformers) are possible for $(TTN)Mo(CO)_3$:



The crystal structure is that of the syn (endo) regioisomer. It is significant that only one methyl resonance is observed in the ^1H NMR. This is consistent with either of the syn regioisomers or with a rapid interconversion of the regioisomers on the NMR time scale.[14,15] Molecular models suggest that both the anti and the syn (exo) regioisomers are sterically demanding. Therefore, we conclude tht only one regioisomer of $(TTN)Mo(CO)_3$ exists.

The S–C–C′–S′ torsion angles in TTCN, TTN, and their complexes provide a more detailed picture of the conformations of the ligands and the effect of metal complexation on the stereochemistry of polythioethers. The observed torsion angles reflect nonbonded repulsions among the sulfur lone pairs and the stabilization of sulfur lone pairs by coordination to the metal. However, before a comparison of these structures is made, a discussion of the nature of thioether lone pairs is appropriate.

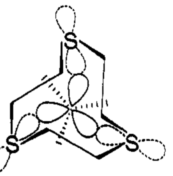
The two lone-pair orbitals of thioether molecules have been described alternatively as equivalent orbitals tetrahedrally disposed about the sulfur atom[2] or as an "s-type" and a "p-type" lone pair.[2,19] However, neither description satisfactorily accounts for the coordination chemistry of thioether ligands. Recent theoretical[20,21] and structural[21] studies indicate that thioethers possess two donor molecule orbitals. The highest occupied molecular orbital (HOMO) of free thioethers is primarily sulfur 3p in character, nonbonding, and spatially localized perpendicular to the R–S–R plane. The second donor orbital is energetically somewhat more stable, also largely sulfur 3p in character, S–R bonding, and localized along the bisector of the R–S–R angle. In C_{2v} symmetry these two thioether donor orbitals belong to the $1b_1$ and $2a_1$ representations, respectively. Upon coordination of a thioether to a metal, the local symmetry at sulfur is reduced from C_{2v} to C_s and the two donor orbitals both belong to the a′ representation and consequently are free to mix (**1a–c**). The extent to which the $1b_1$ and $2a_1$ orbitals mix upon coordination is reflected in the tilt angle between the M–S vector and the bisector of the R–S–R angle. If $1b_1$ and $2a_1$ do not mix and $1b_1$ is the principal donor orbital, then a tilt angle of 90° should result (**1a**). Conversely, if $1b_1$ and $2a_1$ participate equally as donor oribtals, then a tilt angle of 135° should result (**1b**). For comparison, a tilt angle of 125.25° would be expected for a sp^3-hybridized sulfur atom.



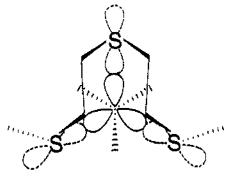
1

Crystallographic data for thioether complexes[2,21] show that the R–S–R bond angles (typically ca. 102°) are not perturbed significantly upon coordination of the thioether and that tilt angles between 105 and 120° (typically ca. 115°) are observed (**1c**). These results indicate that the HOMO ($1b_1$) of the free thioether is the most important ligand donor orbital.[22]

The mixing of the $1b_1$ and $2a_1$ orbitals of the free thioether upon coordination to a metal is conveniently described in terms of two new orthogonal ligand orbitals, which are principally sulfur 3p in character. These new orbitals lie in the plane that is normal to the R_2S plane and that bisects the R–S–R angle. One orbital is approximately σ-donating with respect to the metal, and the other orbital is oriented for potential π-donation to the metal (**1c**). **2a** and **2b** depict the orientation of the σ-donor orbitals of the TTCN and TTN ligands.



2a



2b

In both complexed[3,4] and uncomplexed[16] TTCN the sulfur lone pairs ($1b_1$-type orbitals) are endodentate. The TTCN molecule

---

(14) Difficulties with the solubility of $(TTN)Mo(CO)_3$ prevented the attainment of a low-temperature ^1H NMR spectrum.

(15) The ^{95}Mo NMR spectrum shows a singlet with an exceptionally narrow line width (14 Hz). For an example of isomer detection by ^{95}Mo NMR see: Buchanan, I.; Minelli, M.; Ashby, M. T.; King, T. J.; Enemark, J. H.; Garner, C. D. *Inorg. Chem.* **1984**, *23*, 495.

(16) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

(17) A corresponding rotation about the S1–C5 and S3–C8 bonds must accompany a change in the S–C–C′–S′ torsion angle so as to redirect the p-type sulfur lone pairs toward the metal.

(18) The larger interatomic distance between S1 and S3 is effected by opening up the C6–S2–C7 angle.

(19) Bent, H. A. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977; p 30.

(20) Penfield, K. W.; Gewirth, A. A.; Solomon, E. *J. Am. Chem. Soc.* **1985**, *107*, 4529.

(21) Ashby, M. T. Ph.D. Dissertation, University of Arizona, 1986.

(22) The results of Fenske–Hall molecular orbital calculations on the model compound $Mo(SH_2)(CO)_5$ support the postulate that the principal donor orbital for complexed thioethers is the out-of-plane $1b_1$ orbital.[21] These results are in contrast to SCF-X_α–SW calculations on the blue copper center of plastocyanin, which predict the principal donor orbital of the methionine ligand to be the in-plane $2a_1$ orbital.[20] However, plastocyanin may not be a typical metal–thioether complex because of the unusually long methionine Cu–S bond length (2.90 Å) and obtuse tilt angle (150°).

compensates for the repulsive interactions between the sulfur atoms by increasing the S–C–C′–S′ torsion angle. An increase in this angle effects an increase in the intersulfur distances and also directs the sulfur lone pairs slightly away from the molecule's 3-fold rotation axis. For complexed TTCN the stabilization provided by formation of the metal–sulfur bonds partly overcomes the repulsion between the sulfur atoms. Thus the S–C–C′–S′ torsion angle is smaller, and the intersulfur distance is shorter for the complexed molecule as compared to uncomplexed TTCN. Because the sulfur σ-donor orbitals of complexed TTCN are directed slightly away from the 3-fold axis, a trigonal distortion is observed in the (TTCN)Mo(CO)$_3$ molecule, which is the result of an optimization of the orbital overlap of the thioether σ-donor orbitals with the empty metal acceptor orbitals (**2a**). The S–C–C′–S′ torsion angle also governs the intersulfur distances in (TTN)Mo(CO)$_3$. However, the open chain of TTN leads to S1–C5–C6–S2 and S2–C7–C8–S3 torsion angles, which are of equal magnitude but opposing sign. This stereochemistry permits each σ-donor orbital on sulfur to point directly at the metal atom (**2b**).[17] It is interesting that the magnitudes of the S–C–C′–S′ torsion angles in (TTCN)Mo(CO)$_3$ and (TTN)Mo(CO)$_3$ are similar. As a result, the S1··S2 and S3··S2 interatomic distances in (TTN)Mo(CO)$_3$ are comparable to the average intersulfur distance in (TTCN)Mo(CO)$_3$. However, the S1··S3 interatomic distance in (TTN)Mo(CO)$_3$ is significantly longer. This is likely the result of a repulsive filled–filled interaction between the π-donor orbitals on S1 and S3.[2,18] Finally, the S1–C5–C6–S2 and S2–C7–C8–S3 torsion angles could, in principle, change signs (e.g. S1–C5–C6–S2 = −46.0° and S2–C7–C8–S3 = 48.3°) without affecting the intersulfur distances; however, this torsional change rotates the thioether π-donor orbitals on S1 and S3 toward one another and consequently should be sterically disfavored.

For (TTN)Mo(CO)$_3$, the average Mo distance to S1 and S3 (2.578 (4) Å) is longer than the distance to the central sulfur atom (Mo–S2 = 2.528 (1) Å), which is similar to the average Mo–S distance in (TTCN)Mo(CO)$_3$ (2.52 (2) Å). The longer Mo–S1 and Mo–S3 distances as compared to the Mo–S2 distance in (TTN)Mo(CO)$_3$ may be another consequence of the repulsive filled–filled interaction between S1 and S3 in coordinated TTN (vide supra).

If the thioether σ-donor orbitals in (TTN)Mo(CO)$_3$ are indeed more favorably directed toward the empty metal orbitals than for (TTCN)Mo(CO)$_3$, then TTN should be a better electron donor than TTCN. The slightly lower carbonyl stretching frequencies for (TTN)Mo(CO)$_3$ (ν_{CO}(nitromethane) = 1927, 1815 cm^{-1}) than for (TTCN)Mo(CO)$_3$ (ν_{CO}(nitromethane) = 1935, 1825 cm^{-1}) seem to support this.

Acknowledgment. The crystal structure of (TTN)Mo(CO)$_3$ was solved at the University of Arizona Molecular Structure Laboratory. Financial support of this work by NIH Grant ES 00966 (J.H.E.) and Department of Energy Contract DE-AC0280ER10746 (D.L.L.) is gratefully acknowledged. We also thank Dr. C. G. Young for obtaining the ^{95}Mo NMR spectrum of (TTN)Mo(CO)$_3$.

Registry No. (TTN)Mo(CO)$_3$, 102941-85-5; TTN, 37460-04-1; bis(2-mercaptoethyl) sulfide, 3570-55-6.

Supplementary Material Available: Figure 3, showing a stereoscopic ORTEP drawing of the unit cell, Table VII, listing the anisotropic thermal parameters for the non-hydrogen atoms, and Table VIII, listing the refined positions of the hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Department of Crystallography,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

^{1}H and ^{13}C NMR Spectra of a Series of Methyl-Substituted Imidazole Complexes of Pentaamminecobalt(III) and Crystal Structure of the Remote Isomer of [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate

Wayne W. Henderson,[†] Rex E. Shepherd,*[†] and Jaime Abola[‡]

Received November 22, 1985

The crystal structure for the remote isomer of [(4-methylimidazole)pentaamminecobalt(III)] trichloride dihydrate, $CoC_4H_{21}N_7Cl_3\cdot 2H_2O$, was determined from 1775 reflections (Mo $K\alpha$) to R = 0.04 (R_w = 0.043); the space group is $Pna2_1$. The unit cell constants a, b, and c are 7.011 (2), 10.373 (3), and 21.420 (3) Å; $\alpha = \beta = \gamma$ = 90.0 (0)° (orthorhombic). The number of molecules per unit cell, Z, is 4. Coordination of the 4-methylimidazole ligand occurs via the 5-methylimidazole tautomer, e.g., the remote isomer. The Co–cis-NH$_3$ bond lengths average 1.96 Å, ranging between 1.930 (6) and 1.992 (10) Å; the Co–trans-NH$_3$ band exhibits no discernible trans effect at 1.976 (5) Å. The Co–N(3) (5-methylimidazole) distance is 1.945 (5) Å. The plane of the imidazole ring makes dihedral angles of 43.6 and 41.9° with the Co–cis-NH$_3$ planes. ^{1}H and ^{13}C NMR data for the free ligands and their Co(NH$_3$)$_5$$^{3+}$ complexes are reported for the following L: 1-methylimidazole; 2-methylimidazole; 4-methylimidazole; 5-methylimidazole; 1,2-dimethylimidazole; 1,4-dimethylimidazole; 1,5-dimethylimidazole; 2,5-dimethylimidazole. Ring carbons in the C(2) and C(5) positions show downfield ^{13}C shifts ($\Delta\delta_C$) upon coordination while C(4) carbons exhibit upfield shifts or smaller downfield shifts than C(2) or C(5). Methyl ring substituents follow the shift of their ring carbon or are shifted downfield for N-methylation. The ^{1}H shifts relative to those of the free ligands ($\Delta\delta_H$) show downfield shifts at all ring positions, but the H(4) proton undergoes smaller downfield shifts. The origin of the shifts upon coordination ($\Delta\delta_H$ and $\Delta\delta_C$) are explained on the basis of an induced rehybridization of the ring carbons upon coordination of a withdrawing metal center at N(3) of the imidazole ring.

Introduction

Nuclear magnetic resonance spectroscopy (NMR) has been used to evaluate the changes in electron density within ligands upon coordination to a variety of metals. These electron density changes can occur by σ- and π-electron polarization, which are related to the σ basicity and the π-acceptor ability of the ligand. Complicating the interpretation of the NMR shift values are any of several local effects caused by anisotropy and electron currents within the metal fragments. These factors have been discussed for a range of ligands including organonitriles, pyridines, and diazines and their complexes Co(NH$_3$)$_5$L^{3+}, Ru(NH$_3$)$_5$L^{2+}, Rh(NH$_3$)$_5$L^{3+}, Fe(CN)$_5$L^{3-}, Co(CN)$_5$L^{2-}, and H$^+$.[1,2,9-13]

[†] Department of Chemistry.

[‡] Department of Crystallography.

(1) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718–724.

(2) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Peterson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417–8425.

(3) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754–2763.

0020-1669/86/1325-3157$01.50/0